Chemical Additive Cascading System – A new Scheme for Enhancing Optical Nonlinearity

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ABSTRACT

Nanophotonics is an emerging area where nanotechnology is used to change the physical and chemical properties of photonic materials or the effectiveness of photonic processes that have major applications in optical communication and computation. Though many photonic devices are developed using nonlinear optical materials, efforts are still going on to increase their efficiency toward 100% and other device characteristics toward their optimum level. In order to improve the efficiency of the third harmonic process further, we have a plan to use dye-sensitized metal nanoparticles doped in PMMA films. It is expected that the ability of nanotechnology in tailoring the physio-chemical properties of the materials will give rise to the optimum nonlinear devices to be used in nanophotonics. A considerable improvement in both nonlinear optical susceptibility and laser damage threshold is expected based on the results published in the case of dye-sensitized metal nanoparticle doped solar cells. Such a research may contribute to the efficient nanophotonic devices such as all optical switches, which are the basic building blocks of the final dream of realizing all optical computers. In this paper, a theoretical study is carried out on the effect of sensitization of some well-known nanocomposites TiO_2/Au and ZnS/PVA by nonlinear DASPB dye-doped PMMA-MA polymer matrix in order to change the dielectric and nonlinear susceptibility. This is achieved by the systematic study of the size of nanoparticles used for the sensitization study, various donor-acceptor combinations, and concentration of dyes & nanoparticles in the sample films. The nonlinear absorption coefficient for each case and the theoretical optical limiting properties are expected to be modified based on cascaded nonlinear susceptibility for Type 1, Type 2, and Type 3 Z-scan configurations.

Keywords: Dye-sensitization, Nano-composites, Polymer films, Nonlinear absorption, Optical limiting.

1. INTRODUCTION:

The research in nonlinear optical materials has been active since the last sixty years to identify suitable efficient materials for the third harmonic generation, stimulated scattering, multi-photon absorption, and nonlinear refraction to be used in optical limiting, optical switching, and all optical devices, which have major applications in optical communication and optical computation [1]. Self-focusing materials for light beams with an optimum level of intensity-dependent refractive index to produce the required amount of intensity dependent phase shift in all-optical devices are still in continuous search. Alternatively, nanophotonics is an emerging area where the special properties of materials at the nanoscale is used to change the physical and chemical properties of materials or the effectiveness of photonic processes. In this paper, in order to improve the efficiency of the third harmonic process further, we have proposed a new model to use dye-sensitized metal nanoparticles doped in PMMA films.

Further, many organic materials including dye-doped polymer films are finding potential attraction in this regard due to their advantages in terms of enhanced efficiency, optimum material, and mechanical

properties to fabricate reliable devices [2]. Both nonlinear absorption and nonlinear refraction properties of a material for an input light beam decide its third harmonic generation efficiency. For improving the third order NLO-effects of organic materials, it is found that there is a relationship between electronic structure and molecular geometry, especially the length of the π-system [3]. Whenever an electron excitation occurs, there will be a relaxation of the molecular geometry, which can lead to the formation of nonlinear excitations. It is found that the relaxation of the molecular geometry is much slower than the change in π-electron distribution and it is this instantaneous shift in π-electron density that is responsible for the large and fast polarizabilities of π-electron networks [3]. Thus, by tailoring the molecular geometry, one can modify the polarizability of the molecules and hence third-order optical nonlinearity of the material.

2. RELATED WORK:

It is expected that the ability of nanotechnology in tailoring the physio-chemical properties of the materials will give rise to the optimum nonlinear devices to be used in nanophotonics. A considerable improvement in both nonlinear optical susceptibility and laser damage threshold is expected based on the results published in the case of dye-sensitized metal nanoparticle doped solar cells. Such a research may contribute to the efficient nanophotonic devices such as all optical switches, which are the basic building blocks of the final dream of realizing all optical computers. Table 1 depicts some research results on dye doped polymer films and nanocomposite doped polymers in solar cell research and nonlinear optical materials research.

Table 1: Related scholarly work on nonlinear optical studies on dye-doped polymers and nanocomposite doped polymers

S.No.	Nonlinear Optical System	Material/Focus	Reference
1	Dye-doped polymers	Optical limiting effect of metanil yellow dye in solid media	Rekha, R. K. et al. (2009). [4]
2	Dye-doped polymers	Nonlinear and optical limiting study in Mercurochrome dyes	Krishnamurthy, R. R. et al. (2010). [5]
3	Dye-doped polymers	Nonlinear and optical limiting study in Chicago sky blue 6B dye doped PVA film	Hassan, Q. M. A. (2008). [6]
4	Dye-doped polymers	Optical limiting in Disperse red 1 dye-doped polymer	Zidan, M. D. et al. (2011). [7]
5	Dye-doped polymers	Optical limiting properties of magenta dye-doped PMMA	Manshad, R. K. H. et al. (2012). [8]
6	Dye-doped polymers	Optical limiting studies in disperse orange-25 dye-doped PMMA-MA polymer films	Aithal, S. et al. (2016). [9]
7	Dye-doped polymers	Optical Limiting Study in Disperse Yellow Dye-Doped PMMA-MA Polymer Films	Aithal, P. S. et al. (2016). [10]
8	Dye-doped polymers	Optical limiting properties of phthalocyanines dyes in PMMA thin films	Mathews, S. J. et al. (2007). [11]
8	Nanomaterial doped polymers	Nonlinearities of nanostructured C450 doped polymer thin film	Sadik, Z. S. et al. (2012). [12]
9	Nanomaterial doped polymers	Optical limiting study of silver nanoparticle–embedded polymer film	Porel, S. et al. (2007). [13]
10	Nanocomposite doped polymers	Non-linear optical properties of CdS/PS polymer nanocomposite	Tripathi, S. K. et al. (2015). [14]
11	Dye sensitized, nanocomposite doped polymers	Optical limiting studies of nanostructured Cu doped ZnO–PVA composite thin films	Tamgadge, Y. S. et al. (2016). [15]

12	Nanocomposite doped polymers	NLO properties of Ag nanoparticles and photopolymer nanocomposites based on them	Zulina, N. A. et al. (2017). [16]
13	Nanocomposite doped polymers	Optical limiting studies of nanostructured Cu doped ZnO–PVA composite thin films	Tamgadge, Y. S. et al. (2016). [17]
14	Nanocomposite doped polymers	High-performance all-optical limiting based on nonlinear refraction of metal-doped PbS/PVA freestanding nanocomposite films	Rahma, M. A. et al. (2018). [18]
15	Nanocomposite doped polymers	Nonlinear absorption enhancement of AuNPs based polymer nanocomposites	Zulina, N. A. et al. (2018). [19]
16	Dye sensitized, nanocomposite doped polymers	D–A type polyoxometalate/reduced graphene oxide nanocomposite for the photoanode of dye-sensitized solar cells.	Shan, C. H. et al. (2016). [20]
17	Dye sensitized, nanocomposite doped polymers	ZnO: Ag and TZO: Ag plasmonic nanocomposite for enhanced dye sensitized solar cell performance	Tripathi, S. K. et al. (2015). [21]
18	Dye sensitized, nanocomposite doped polymers	Nano-structured TiO2/ZnO nanocomposite for dye-sensitized solar cell application	Boro, B. et al. (2018). [22]

3. OBJECTIVES & METHODOLOGY:

(1) To explore the possibility of improving nonlinear coefficients of the presently available materials
(2) To identify the possibility of using nanocomposites to alter nonlinear susceptibility
(3) To evaluate some of the nanocomposites to be doped in dye sensitized polymer films
(4) To provide theoretical solutions of the chosen nanocomposites in a nonlinear dye sensitized neutral polymer film.
(5) To provide recommendations to the material scientists to conduct experimental investigation to explore the possibility of improvement.
The methodology is theoretical predictive analysis using the reported data and information from various experimental sources.

4. DYE DOPED POLYMERS FOR THIRD ORDER OPTICAL NONLINEARITY:

The optical third harmonic nonlinearity in organic materials generally originated by two photons and multiphoton absorption, two photon florescence, excited state absorption, reverse saturation absorption, thermal lensing effect, etc. Reports show that there has been less work carried on the study of nonlinearities of dyes in solid medium. It is expected that by studying nonlinear properties of dyes in solid medium and identifying active and efficient nonlinear dyes for low power CW laser beams, one can fabricate new elements/components, which have potential applications in optical limiting and optical switching.

5. SCHEMES FOR THE INCREASE OF NONLINEAR SUSCEPTIBILITY:

There are different schemes used to improve the nonlinear optical properties of materials. This includes
(1) Use of organic materials, which show better nonlinear optical properties in some cases due to large nonlinear optical susceptibility and the possibility of tailoring the properties [23].
(2) A-π-A type molecules are the most efficient TP absorbers and hence show high nonlinear absorption properties which can be further tailored as per requirement for different applications [24].
(3) Doping: Introduction of an active material as impurity in a base material to modify the electrical, optical and structural properties. Organic molecules like dye molecules are doped with polymer base to

change the nonlinear optical properties of polymers. For example, rhodamine 6G is doped in Poly (methyl methacrylate) (PMMA) to modify the nonlinear fluorescence emission properties [25].
(4) Sensitizing: Sensitizing is a process of adding organic materials like dyes to the surface of crystals or glass or polymers to make them sensitive to a particular region of the light spectrum. For example, silver halide crystals of photographic emulsions are made to light sensitive in green, red, or infrared regions by sensitizing using some organic dyes [26].
(5) Cascading: By cascading many limiting elements in a single geometry, one can decrease the activating threshold and damage threshold, while increasing the limiting bandwidth. The cascaded optical limiter shows a low activating threshold, a high optical damage threshold, and broadband limiting properties [27].

6. EFFECT OF DOPING NANOCOMPOSITES TO DYE SENSITIZED POLYMER FILMS :

Nanoparticles to be doped and nonlinear dyes to be used to sensitize the polymer films are ZnS, ZnSe, CdSe, Ag, Au, Pt, Al, etc. and the nano-composites to be prepared and used for doping and nonlinear dyes for sensitization are TiO_2/Au ZnS/PVA, Graphite/PVA, Ag/methyl orange etc. The nanoparticles and nanocomposites will be prepared using standard chemical synthesis methods & Green Extract methods.

7. IDEAL OPTICAL LIMITER:

An ideal limiter is a device, which shows linear transmission characteristics below a threshold level and fixes the output to a constant level above it, thus providing safety protection to sensors or human eyes [28]. An ideal optical limiter is a photonic device or component, which has ideal optical limiting characteristics. It can take any intensity input laser beam both continuous wave (CW) or pulsed wave of any time duration. It must process such an incident light beam internally using nonlinear properties of the medium and provide output laser beam of constant intensity or fluency. The ideal optical limiter has the characteristics shown in Figure 1. It has a high linear transmission for low input (e.g., energy E or power P), variable limiting input E or P, and a large dynamic range defined as the ratio of the E or P at which the device gets damages (irreversibly) to the limiting input. Such devices can also be used as power or energy regulators. However, since the primary application of the optical limiter is for sensor protection, and damage to detectors is almost always determined by fluence or irradiance, these are usually the quantities of interest for the output of the limiter. Getting the response of ideal limiter at least above a certain minimum input energy turns out to be possible using a wide variety of materials, however, it is very difficult to get the limiting threshold as low as is often required and at the same time have a large dynamic range. Because high transmission for low inputs is desired, the limiter material must have low linear absorption. Some of the characteristics predicted for ideal limiter are [28] :
(1) An ideal limiter device should be capable of taking input light beam of any intensity without any material damage.
(2) An ideal limiter device should be capable of accepting input light beam without any reflection or scattering from the incident surface.
(3) Any variation in the input intensity or power between zero to infinity should maintain constant output intensity irrespective of input intensity variations.
(4) An ideal optical limiter shows linear transmission characteristics below a threshold level and fixes the output to a constant level above it.
(5) The transmission characteristics of an ideal limiter vary depending upon the incident intensity due to nonlinear properties of the limiter material.
(6) The output intensity/fluency of ideal optical limiter is independent on the wavelength and pulse duration of the laser beam.
(7) An ideal optical limiter should limit the input light of wavelength throughout the electro-magnetic spectrum. i.e., it should have infinite bandwidth.
(8) The nonlinear material medium used for the fabrication of ideal limiter should have high nonlinearity for the entire bandwidth.
(9) The nonlinear material medium used for the fabrication of ideal limiter should limit any laser beam of any power of both CW and pulsed.
(10) An ideal limiter should provide a constant output in any environmental conditions like changes in temperature, pressure, and aging.

(11) The construction of an ideal limiter should be easy and of low cost.

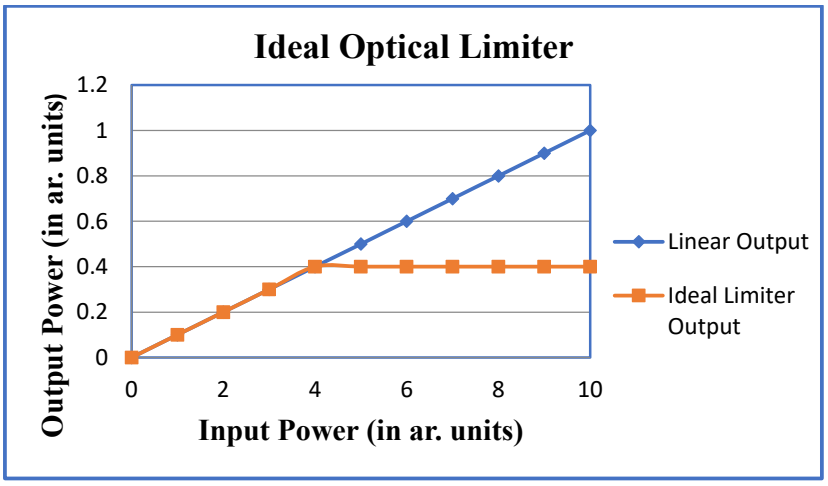

Fig. 1: Input-output characteristics of an ideal optical limiter [28].

The ultimate objective of any optical nonlinear materials research is to find a suitable material which can show optical limiter characteristics close to ideal optical limiter characteristics. Thus, an optimum practical limiter is a device which shows linear transmission characteristics below a threshold level and fixes the output to a constant level above it, thus providing safety protection to sensors or human eyes [28]. The general demands on practical optical limiting device are :

(1) Fast nonlinear response (picoseconds or femtoseconds)
(2) Quick recovery (milliseconds)
(3) High attenuation (more than 90% at limiting wavelength)
(4) Broad frequency band response (in the entire visible region)
(5) Large dynamic range (defined as EL/ED)
(6) High damage threshold (>MW/cm^2)
(7) High linear transmission at low energies (> 80%)
(8) Low light scattering in the material medium

8. THEORETICAL STUDY ON DYE-SENSITIZATION ON NANOCOMPOSITE DOPED POLYMER FILM ON NONLINEAR SUSCEPTIBILITY:

The Z-scan technique is used to study the nonlinear optical properties of the sample [29-30]. The linear absorption coefficient α_0 is determined for the chosen wavelength 532 nm by using formula $\alpha_0 = -\frac{1}{t}\ln\left[\frac{1}{T}\right]$ ---------- (1)

where (t) is the thickness of the sample and T is the transmittance.

The refractive index n_0 can be found from the transmittance spectrum of the film according to the following equation

$n_0 = \frac{1}{T} + \left[\left(\frac{1}{T^2} - 1\right)\right]^{½}$ -------- (2)

The nonlinear absorption coefficient β can be estimated from the open aperture Z-scan data, where $\beta = (2\sqrt{2}\,\Delta T) / (I_0 L_{eff})$ ----- (3)

I_0 is the intensity at the focal spot given by $I_0 = 2P_{peak}/\pi\omega_0^2$ --------- (4)

The effective length of the sample can be determined from the formula $L_{eff} = (1 - e^{-\alpha_0 L})/\alpha_0$ ------- (5)

The transmittance increases with increasing excitation intensity and has a maximum value at the focus, which is the signature of saturation absorption according to Sheik-Bahae's theory. When saturation absorption occurs, the absorption coefficient β is no longer a constant. Instead, it becomes a function of the excitation intensity as in the relation,

$\alpha = \alpha_0 + I\beta$ ------- (6), where α_0 is the linear absorption coefficient, α is the total absorption coefficient,

β is the nonlinear absorption coefficient, and I is the incident intensity of the laser beam.
In the simplest case, when only third-order nonlinearities are considered in the sample, the resultant change in refractive index becomes: $n = n_0 + n_2 I$. -------- (7)
where n is the total refractive index of the sample, n_0 is the linear refractive index of the sample, n_2 is the third-order nonlinear refractive index of the sample, and I is the excitation intensity.

The major common processes which support optical limiting in case of a nonlinear material are (1) Two photon absorption (TPA), (2) Reverse saturable absorption (RSA), (3) Nonlinear refraction (NR), (4) Induced scattering (IS), and (5) Photorefraction (PR).
It is known that TPA is an instantaneous and important process for optical limiting. But due to low β values for most of materials, only TPA is not enough to function as a satisfying optical limiter so that a scheme of combining other processes like RSA, NR, IS, and PR may give rise to favourable result on increasing optical nonlinearity. This is a new version of additive-cascaded nonlinearity. In cascaded nonlinearity, the internal processes are divided into two groups. The first group supports simultaneous action two or more sub-processes occurring cascaded media, originated due to changes in certain parameters of light wave like amplitude, phase, beam size, polarization state, etc. The second group supports the generation of new light wave due to cascaded interaction. In our proposed new scheme using a cascaded system principle, additive interactions due to Two photon absorption (TPA), Reverse saturable absorption (RSA), nonlinear refraction (NR) and induced scattering (IS) are to be achieved simultaneously. This can be achieved simultaneously using internal additive cascading method (chemical method) or external additive cascading method (physical method).
By cascading many limiting elements in a single geometry, one can decrease the activating threshold and damage threshold, while increasing the limiting bandwidth. The cascaded optical limiter shows a low activating threshold, a high optical damage threshold, and broadband limiting properties [27].

(1) Two photon absorption (TPA):

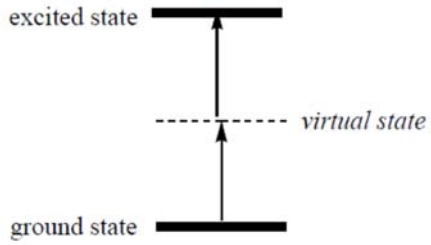

Fig. 2: Schematic diagram representing TPA.

The TPA coefficient, β, is related to the imaginary part of χ3 through the eqn.
$\beta = (3\omega / 2\varepsilon_0 c^2 n^2_0) \mathrm{Im}[\chi^3]$ ------- (8)
Where ω is the circular frequency of the light, ε_0 is the dielectric constant, c is the speed of light in vacuum and n_0 is the linear index of refraction. For a material that is transparent at low intensities, α = 0, the change in the intensity of the light propagating through a material is thus given by eqn.
$I(L) = I_0 / (1+I_0 \beta L)$ ---------- (9)
Where L is the sample length and I_0 is the incoming intensity. This equation shows that the transmission decreases as the intensity, I_0, increases. The decrease in the transmission is, thus, correlated with the TPA coefficient, intensity and material thickness. However, most materials possess a rather small β value, which means that the intensity must be very high in order to see any optical limiting effect due to TPA.

(2) Reverse saturable absorption (RSA):

Reverse Saturable Absorption (RSA) is a property of materials where, the absorption if light increases with increasing light intensity. Materials in which the excited state absorption is large compared to the ground state absorption can undergo a process called reverse saturable absorption (RSA).
Bleachable dyes are molecules whose absorption can be saturated by high intensity light. Such a material will absorb light until the ground state is depleted of electrons, where after the transmission for

a short time will be close to 100 %. The dye will then relax back to its ground state when the light is removed. This process is called saturable absorption and is outlined in figure 3 :

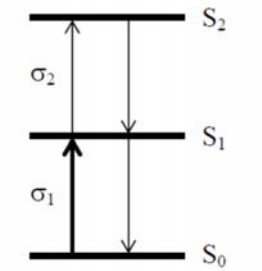

Fig. 3 : Electronic process of two energy level SA.

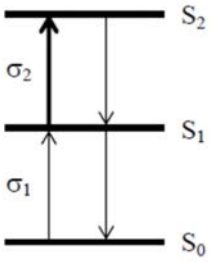

Fig. 4: Three energy level model of RSA

Reverse saturable absorption or reversed bleaching can be observed in materials that absorb more in the excited state than in the ground state. As the intensity increases, the absorption increases and transmission decreases. The simplest model to describe this is the three-level model outlined in figure 4. The ground state cross section is denoted σ_1, and the exited state cross section σ_2. As the material absorbs light the first excited state, S_1, is populated. If σ_2 is smaller than σ_1 the material will be more transparent as the ground state is depleted of electrons and bleaching will occur. If, on the other hand, σ_2 is larger than σ_1, absorption will increase as S_1 is populated and reversed saturation absorption occurs.

(3) Nonlinear refraction (NR):

When a nonlinear optical (NLO) material, also called optical limiting (OL) material is subjected to light of high intensity it may demonstrate a change in refraction index [10]. This change can be seen as either positive or negative and cause the material to either defocus or focus the light, as illustrated in the following figure 5.

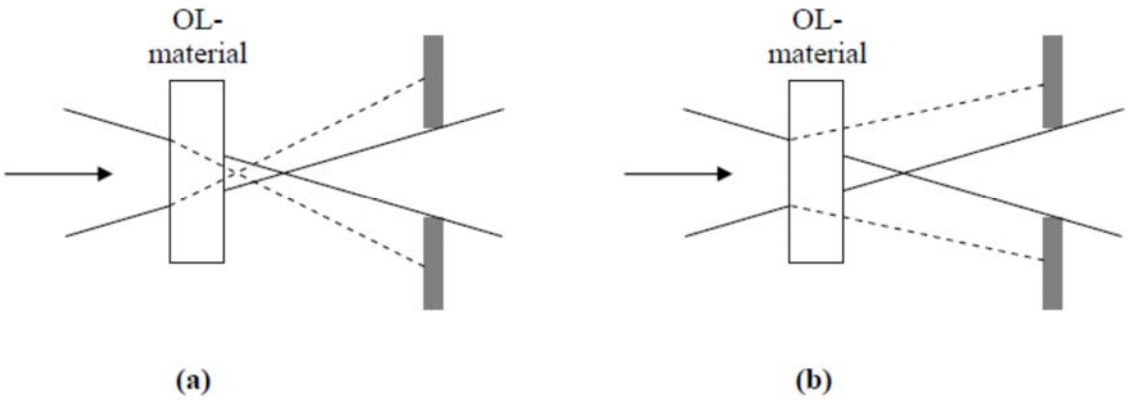

Fig. 5: Nonlinear refraction (a) Self-focusing, (b) Self-defocusing [10]

As seen from figure 5, both self-focusing and self-defocusing materials will refract the light away from the optical sensor and thus act as an optical limiter. A self-defocusing material has the advantage of

leading the light away from the beam axis and thus can be regarded as self-protecting, in contrast to a self-focusing material which will suffer a great risk of damaging. On the other hand, a self-focusing material will be able to activate itself at a lower energy input compared to a self-defocusing matter, and an optical limiting device based on non-linear refraction will generally, independent of sign, exhibit a larger dynamic range than devices based on absorption alone. Nonlinear changes of refraction in a material can be a result of both instantaneous and accumulated processes.

(4) Induced scattering (IS):

If the intensity of the incident light is very high like in the case of laser beam, nonlinear effects appear in the medium. The microscopic particles or nanoparticles of the medium are affected not only by forces with frequencies of the incident ω and scattered ω′ radiations but also by a force acting at the difference frequency Δω—that is, at the frequency of the microscopic particles' natural vibrations—which leads to resonance excitation of vibrations. This leads to an increase in the intensity of scattered light, which further reinforces the vibrations of micro/nanoparticles and so on and it leads to stimulated scattering. The intensity of the scattered light during induced light scattering may be on the order of the incident light intensity. The scattering could cause polarization dependent loss and change the polarization state of the light in devices.

(5) Photorefraction (PR):

Photorefraction is a kind of nonlinearity exhibited by certain types of materials which generally shows linear or quadratic optical properties. Photorefraction is observed when the material is illuminated by a two-beam interference pattern, which generates a photoinduced charge distribution. This allows trapping of photo-generated carriers (electrons or holes) and gives rise to a space-charge field in the volume of the material, which modulates the refractive index through the electro-optics coefficient. Photorefractive materials such as $LiNbO_3$, $BaTiO_3$, and $Bi_{12}(Si,Ge,Ti)O_{20}$, semiconductors such as GaAs, InP, and CdTe, PLZT ceramics, doped EO polymers, and liquid crystals have shown photorefractive properties [31].

9. CHEMICAL ADDITIVE CASCADING SYSTEM (CACS) MODEL:

In our proposed new scheme using a cascaded system principle, additive interactions due to Two photon absorption (TPA), Reverse saturable absorption (RSA), nonlinear refraction (NR) and induced scattering (IS) are to be achieved simultaneously. This can be achieved simultaneously using internal additive cascading method (chemical method) or external additive cascading method (physical method) as shown in figure 6 [32-33]. In this section, we have used internal additive cascading method which is a chemical method to make use of TPA, RSA, NR, and IS simultaneously by proposing some nonlinear dye sensitized, nanocomposite doped polymer film system. This scheme is named as chemical additive cascading system (CACS) to enhance optical nonlinearity in any photonic system where the total third-order nonlinear optical susceptibility will be expected as the sum of individual chemical processes. Chemical cascading is an inhomogeneous mixture of different individual chemicals and in this model, it is postulated that they add their nonlinearity individually to the whole system as depicted in figure 7. It is noted that the active medium in chemical cascading consist of inhomogeneous mixture of chemicals which have different nonlinear optical properties like two photon absorption, reverse saturation absorption, nonlinear refraction, or induced scattering. It is also postulated that the components of the mixture will not chemically react to form new chemically homogeneous material.

Advantages of the CACS scheme :

(1) Chemical additive cascading system is an additive system where third-order nonlinear susceptibility will be close to the sum of third order nonlinear susceptibilities of individual ingredients.
(2) Adding different types of nonlinearities in a single system to take the advantages of individual subsystems.
(3) Chemical cascade system avoids scattering of light to different directions compared to physical cascading (figure 6) where the light reflects and scatters when it passes from one compartment to another in the cascaded system.
(4) The cascaded optical limiter shows a low activating threshold.
(5) The cascaded optical limiter shows a high optical damage threshold.

(6) The cascaded optical limiter shows broadband limiting properties.

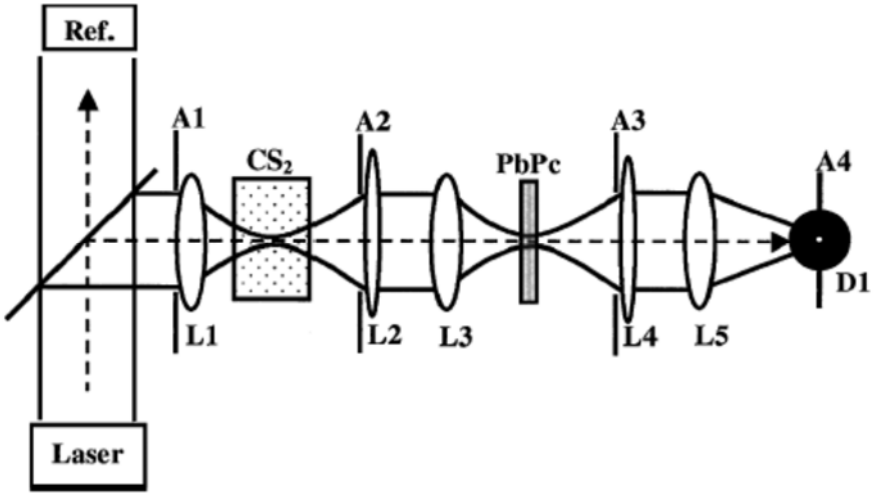

Fig. 6: External additive cascading method (physical method) [33]

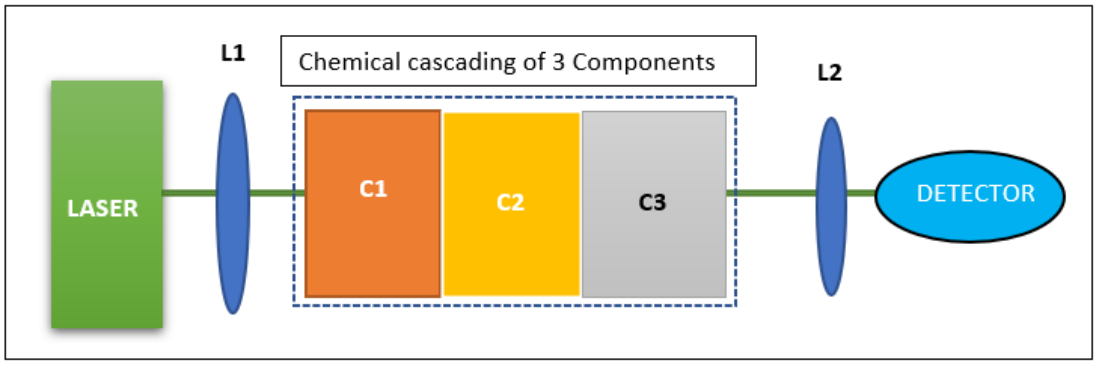

Fig. 7: Schematic representation of CACS Model of Cascading 3 components

10. EFFECT OF VARIOUS PARAMETERS ON NONLINEAR SUSCEPTIBILITY :

The effect of size of nanoparticles used as a dopant, nanoparticles in the sample films, various donor-acceptor molecular combinations in the organic dyes, and concentration of dyes etc. are studied theoretically using third order nonlinear optical susceptibility relations. The variation in the nonlinear absorption coefficient at 532 nm wavelength laser light beam are calculated in each case and the nonlinear susceptibility is estimated using Type 1, Type 2, and Type 3 Z-scan configurations [9].

11. THIRD-ORDER NONLINEAR OPTICAL SUSCEPTIBILITY $|\chi^{(3)}|$:

The Z- scan plot of DASPB dye in PMMA-MA polymer film, show a pre-focal transmittance minimum (valley) followed by a post-focal transmittance maximum (peak). This indicates that DASPB has a positive non-linearity due to self-focusing. Self-focusing is due to variation in refractive index with the two-photon absorption or/and reverse saturation absorption. The nonlinear refractive index n_2 can be calculated using equation (9) and the change in the refractive index, Δn can be calculated using equation (5.8). Experimentally determined nonlinear refractive index n_2 can be used to find the real part of the third-order nonlinear optical susceptibility [χ^3] according to the following relation [30, 34],

$$\text{Re } \chi^{(3)} = |\chi^3| = \frac{10^{-4}\,\epsilon_0\,(n_0^2)c^2\,n_2}{\pi} \quad (\text{cm}^2/\text{W}) \quad \text{--------- (10)}$$

Experimentally determined nonlinear absorption coefficient β can be used to find the imaginary part of the third-order nonlinear optical susceptibility [χ^3] according to the following relation

$$\text{Im } \chi^{(3)} = \frac{10^{-2}\,\epsilon_0\,(n_0^2)c^2\,\lambda}{4\pi^2} \quad (\text{cm}^2/\text{W}) \quad \text{--------- (11)}$$

The absolute value of the third-order nonlinear optical susceptibility is given by the relation

$| \chi^3| = [(\text{Re } \chi^{(3)})^2 + (\text{Im } \chi^{(3)})^2]^{½}$ --------- (12)

Where ϵ_0 is the vacuum permittivity and c is the velocity of light in vacuum.

The nonlinear parameters such as nonlinear refractive index (n_2), change in refractive index (Δn), nonlinear absorption coefficient (α) and nonlinear susceptibility ($\chi^{(3)}$) are calculated and listed in Table 2.

Table 2: Parameters of Nonlinear dyes in PMMA-MA film of thickness 10 µm, and dye concentration 5mM.

S. No.	Dye Material	$\chi^{(3)}$	Nonlinear Chemical Process	Reference
1	DASPB	13.5 x 10^{-6} esu	Two photon absorption	Shubrajyotsna Aithal et al. (2017). [35]
2	DO-25	9.7 x 10^{-6} esu	Reverse Saturation absorption	Shubrajyotsna Aithal et al. (2017). [36]
3	DY-7	8.5 x 10^{-6} esu	Reverse Saturation absorption	Shubrajyotsna Aithal et al. (2017). [37]

Table 3: Parameters of ZnO Nanocomposites in PMMA-MA film of thickness 10µm, and concentration 5 mM.

S. No.	Nanocomposite Material (100 nm)	$\chi^{(3)}$	Nonlinear Chemical Process	Reference
1	ZnO	1.7 × 10^{-12} esu	Induced Scattering	Liu, C. Y. et al. (2004). [38]
2	ZnO/PMMA-MA	6.0 × 10^{-11} esu	Induced scattering & Reverse Saturation absorption	Kulyk, B. et al. (2009). [39]
3	PMMA	3.0 × 10^{-14} esu	Nonlinear absorption	D'Amore, Franco et al. (2004). [40]
4	DASPB/ ZnO/PMMA-MA (Present proposal)	(6.0 × 10^{-11} esu + 13.5 x 10^{-6} esu)	Induced scattering, Two Photon Absorption & Reverse Saturation absorption	Present work*

Table 4: Parameters of Au Nanocomposites in PMMA-MA film of thickness 10µm, and concentration 5mM.

S. No.	Nanocomposite Material (100 nm)	$\chi^{(3)}$	Nonlinear Chemical Process	Reference
1	TiO_2/Au	3.0 × 10^{-9} esu	Induced Scattering	Wang, Q. et al. (2005). [41]
2	Au/PMMA-MA	4.0 × 10^{-9} esu	Induced scattering & Reverse Saturation absorption	Torres-Cisneros, M. et al. (2009). [42]
3	PMMA	3.0 × 10^{-14} esu	Nonlinear absorption	D'Amore, Franco et al. (2004). [43]
4	DASPB/Au/PMMA-MA (Present proposal)	(7.0 × 10^{-9} esu + 13.5 x 10^{-6} esu)	Induced scattering, Two Photon Absorption & Reverse Saturation absorption	Present work*

Table 5: Additive nonlinearity of Dye sensitized and Nanocomposites doped in PMMA-MA film of thickness 10 µm, and concentration 5 mM.

S. No.	Cascaded System	$\chi^{(3)}$ (ZnO/PMMA)	$\chi^{(3)}$ (Dye)	Total $\chi^{(3)}$

1	DASPB + Zn/PMMA-MA	6.0×10^{-11} esu	13.5×10^{-6} esu	(6.0×10^{-11} esu + 13.5×10^{-6} esu)
2	DO-25 + Zn/PMMA-MA	6.0×10^{-11} esu	9.7×10^{-6} esu	(6.0×10^{-11} esu + 9.7×10^{-6} esu)
3	DY-7 + Zn/PMMA-MA	6.0×10^{-11} esu	8.5×10^{-6} esu	(6.0×10^{-11} esu + 8.5×10^{-6} esu)

12. OPTICAL LIMITING STUDY:

Based on the argument of additive nonlinearity, the theoretical transmittance against input power of the two additive sample systems should get modified due to enhanced nonlinear susceptibility. This should be true if both possess positive nonlinearity or both possess negative nonlinearity. Further, if the cascaded samples have opposite nonlinearity, i.e., positive and negative, the resultant system will show the difference and hence decreased nonlinear susceptibility. Thus, a chemical additive cascading system (CACS) is expected to enhance optical nonlinearity in any photonic system if the component systems have the same type of nonlinearity (positive or negative) where the total third-order nonlinear optical susceptibility will be expected as the sum of individual chemical processes.

The nonlinear absorption coefficient for each case of cascaded nonlinear system for any combination of the same type of nonlinearity to be used for optical limiting purposes due to the resultant nonlinear susceptibility can be estimated using Type 1, Type 2, and Type 3 Z-scan configurations [9, 10]. These are passive optical limiters and based on the position of the nonlinear material on the focus point, away from the focus point toward the detector side, and away from focus point with respect to detection side are classified into Type 1, Type 2, and Type 3 optical limiting configurations, respectively. Type 1 optical limiter make use of nonlinear absorption properties of the limiting material, Type 2 optical limiter make use of nonlinear refractive defocusing property of the limiting material, and Type 3 optical limiter make use of nonlinear refractive focusing property of the limiting material. It is expected that, in all three cases, cascaded chemical additive nonlinearity concept should show better results either by showing tailored cut-off frequency for saturation or by showing larger bandwidth for saturation, both improve the properties of practical optical limiters. A systematic experimental study on chemical cascading to enhance or control additive nonlinearity is underway to prove this newly predicted scheme.

13. SUGGESTION & CONCLUSION:

Based on the predicted model of chemical cascading, the nonlinear optical susceptibility of the system consisting of either positive nonlinear components or negative nonlinear components can be improved theoretically and hence the nonlinear optical susceptibility can be tailored according to the need of optical limiting application. The resultant cascaded optical limiting system may have improved limiting cut-off frequency or saturated output bandwidth. It can be further proposed that such chemical cascaded nonlinear optical systems with many chemical components can be used for all three types (Type 1, Type 2, and Type 3) of optical limiting configurations for device applications.

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